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Genetic and chemical modification of cells for selective separation and analysis of heavy metals of biological or environmental significance

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ABSTRACT

Bioaccumulation describes the ability for microbes or other biological cells to accumulate heavy-metal species from the ambient environment. It has attracted extensive attention in the field of heavy metal remediation and precious metal recovery. Bioaccumulation has also shown great potential for adsorption and preconcentration of ultra-trace levels of heavy metals for their analysis and speciation. Genetic engineering and chemical modification of biological cells open up new avenues for bioaccumulative preconcentration of heavy-metal species for selective analysis and speciation of such metals in combination with spectrometric techniques. We focus on recent progress in genetic and chemical approaches to bioremediation and their applications in selective preconcentration and speciation of heavy-metal species. We also outline the uptake mechanisms of bioaccumulation and key issues in the biosorption of heavy metals and their analysis and speciation. Finally, we discuss future perspectives in the bioaccumulation of heavy-metal species and their analysis and speciation.

Contents

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1. Introduction

Bioaccumulation, known as the process to adsorb and to accumulate metal species by biological substrates, such as microorganisms, plant residues and agricultural waste, is a promising approach for selective binding of metals and metalloids, including radionuclides. Ever since its discovery, bioaccumulation has attracted extensive attention and been widely used in effluent treatment and precious-metal recovery. The vast potential of biosorbents in separation, preconcentration and speciation of trace-metal species has also been demonstrated, based on the interactions of metals with functional groups on the sorbents.

As novel materials for heavy-metal adsorption and extraction, biosorbents possess a lot of advantages (e.g., wide availability, low cost, sufficient binding sites and high adsorption capacity) [1]. Meanwhile, biosorbents can selectively bind to heavy-metal species in the presence of alkalis or alkaline metals, and even distinguish the toxicity of different metal species [2]. However, the diversity of various binding sites on certain biosorbents leads to low selectivity towards metal species, which becomes the bottle neck of a "selective" bioaccumulation process. It is therefore crucial to improve the selectivity of biosorbents or biological cells and to develop new recognition methods for specific metal species of biological or environmental significance, based on the manipulation of surface properties of biosorbents or cells.

Chemical modification and genetic engineering can artificially manipulate the components of the surface of cells, so they can effectively enhance the adsorption capacity and selectivity towards target-metal species. Chemical modification was extensively employed for improving the sorption capacity of heavy metals, especially anionic metal species, by functionalizing biosorbents with selective moieties. This approach also facilitates metal speciation by manipulating the affinity between biosorbents and metal species. With the fast development of molecule-cloning techniques, genetic engineering has become a routine procedure in conventional laboratories. It opens a door to the manipulation of biological-cell surfaces and to the development of highly-selective approaches to adsorption for heavy-metal species. A typical analytical application of genetic engineering is the whole-cell biosensor based on its selective response to metals of a microorganism-impregnating metal-recognition or regulatory gene [3]. Another is the selective isolation and enrichment of heavy-metal species using genetically-modified (GM) microorganisms as the retention medium. The development of the former approach is mainly restricted by the strict requirement of cell vitality [4], while the latter is much more flexible and has thus gained extensive attention. The capability of genetic engineering to enhance sorption capacity and selectivity towards target-metal species has already been confirmed in bioremediation. Although biosorbents have shown promising potential in analytical sciences, so far there have not been many relevant investigations.

In the following, we highlight recent developments of genetic and chemical manipulation of biological cells for the improvement of sorption capacity and selectivity for heavy-metal species. We focus special attention on the selective preconcentration and speciation of heavy-metal species. In addition, we outline the sorption mechanisms of bioaccumulation and the key issues in the uptake or the binding of heavy metals and their analysis and speciation. Finally, we outline future perspectives in the bioaccumulation of heavy-metal species and their analysis and speciation in biological and environmental sciences.

2. Heavy-metal uptake by organisms or biological cells

2.1. Heavy-metal-uptake mechanisms

The uptake of heavy metals by organisms or biological cells can be categorized into two main processes:

- metabolism-independent biosorption, which mainly happens on the surface of cells; and,
- metabolism-dependent bioaccumulation, including sequestering, redox reaction and species-transformation processes [1,5].

Metal uptake by living cells generally involves both processes, while interactions between dead cells and metal cations take place only on the cell surface (i.e., biosorption is the main mechanism for metal uptake by dead cells). In most biosorption operations, the recovery of retained metal species from biological cells is required, so the intracellular accumulation of metals should be avoided. In practice, the metabolism-dependent uptake process by living cells is usually prevented by deactivating the cells before performing biosorption.

Biosorption or passive sorption mainly happens on the surface of cells (i.e., cell walls or cell membranes). The mechanism of biosorption consists of electrostatic interaction, ion exchange, surface complexation, redox process and precipitation. For most cases, the binding of heavy metals on the cell surface is the result of multi-mechanisms. Since biosorption is metabolism independent, it is usually a fast process that could reach equilibrium within a few minutes or less [3].

Electrostatic interaction is the first step of biosorption. The metal cation is first attracted by functional groups on the cell surface and then further bonded through other driving forces. Electrostatic interaction depends greatly on the acidity of the reaction medium, since the charge property of metal species and the cell surface varies at different pHs [6,7]. A decrease in pH facilitates adsorption of anionic metal species due to protonation of functional groups on the cell surface, such as -NH_2, whereas an increase of pH leads to dissociation of H^+, resulting in a negatively-charged cell surface that is more suitable for the binding of metal cations.

It has been demonstrated that the metal-biosorption process always takes place along with the release of other ions (i.e., an ion-exchange mechanism is involved during this process) [8]. This phenomenon is especially remarkable in the surface of algae. The release of calcium was reported during the binding of cadmium on dealginated seaweed. Displacement of calcium by cadmium occurs with a ratio of 1:1, indicating that ion exchange is the main mechanism for cadmium biosorption.

Surface complexation is another driving force for heavy-metal biosorption. The cell wall is the first location for heavy-metal biosorption; its structure and chemical environment directly determine the biosorption capacity towards certain metals [5]. The cell wall mainly consists of peptidoglycan, polysaccharide and lipid, which are rich in metal-binding ligands (e.g., -COOH, -OH, -HPO_4^{2-}, SO_4^{2-} -$RCOO^-$, $R_2OSO_3^-$, -NH_2 and -SH). Among these functional groups, amine can be more effective in metal uptake, as it binds to anionic metal species via electrostatic interaction and cationic metal species through surface complexation.

Once heavy metals penetrate inside cells through the ion channel, the cells will activate some detoxification systems, by immobilization or efflux [9]. Metal ions can be immobilized by an organelle,